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TITLE: PREPARATION OF NICKEL BASE HIGH CHROMIUM ALLOY EXCELLENT
              IN STRESS, CORROSION CRACKING RESISTANCE

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ABSTRACT:

   PURPOSE: To obtain the titled alloy in which excellent stress corrosion
cracking resistance is not lowered by welding or SR treatment after welding, by
a method wherein the **cold working** ratio of a 30% **Cr**-60% **Ni** type alloy after hot
working is increased and low temp. long-term **annealing** within a specific range
is carried out as final **heat** treatment.

   CONSTITUTION: An alloy containing, on the basis of %, 0.04 or less **C**, 1.0 or
less **Si**, 1.0 or less **Mn**, 0.03 or less P, 0.005 or less S, 50∼80 **Ni**,
15∼35 **Cr**, 0.50 or less Al, in addition, 0.5∼2.0 Mo and/or 0.5∼2.0 W
and, according to necessity, 0.2∼1.0 Ti and comprises the remainder of
substantially Fe is subjected to hot rolling and, after **cold rolling** is carried
out at a working ratio of 38%, final **annealing** is successively carried out
under the **heating** temp. and the **holding** time conditions within a range
encircled by straight lines connecting points A, B, **C**, D and E in the drawing.
In this case, when a **cold working** ratio is increased, an extremely large amount
of slip bands are generatd in the alloy, and therefore, if **annealing** is carried
out at 850°**C** or less remarkably lower than a conventional temp., a large
amount of carbide in the alloy can be finely dispersed and precipitated in
grain within a short time in an opposite manner as compared with a conventional

method.

㊴耐応力腐食割れ性にすぐれたニッケル基高クロム合金の製造方法

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明　　細　　書

1. 発明の名称

　耐応力腐食割れ性にすぐれたニッケル基高クロム合金の製造方法

2. 特許請求の範囲

(1)　C 0.04％以下、Si 1.0％以下、Mn 1.0％以下、P 0.03％以下、S 0.005％以下、Ni 50％～80％、Cr 15～35％、Aℓ 0.50％以下で、必要に応じTi 0.2～1.0％を含み、残部は実質的にFeからなる合金を、熱間加工後、加工率38％以上で冷間圧延し、引き続き添付図面の第1図に示すA(0.5、850)、B(0.5、750)、C(10、675)、D(100、675)、E(100、850)の5点を結ぶ直線で囲まれる範囲内の、加熱温度及び保持時間で最終焼鈍を行うことを特徴とする耐応力腐食割れ性にすぐれたニッケル基高クロム合金の製造方法。

(2)　C 0.04％以下、Si 1.0％以下、Mn 1.0％以下、P 0.03％以下、S 0.005％以下、Ni 50～80％、Cr 15～35％、Aℓ 0.50％以下で、Mo 0.5～2.0％、W 0.5～2.0％ の一方または双方を含有しさらに必

要に応じTi 0.2～1.0％を含み、残部は実質的にFeからなる合金を、熱間加工後、加工率38％以上で冷間圧延し、引き続き添付図面の第1図に示すA(0.5、850)、B(0.5、750)、C(10、675)、D(100、675)、E(100、850)の5点を結ぶ直線で囲まれる範囲内の加熱温度及び保持時間で最終焼鈍を行うことを特徴とする耐応力腐食割れ性にすぐれたニッケル基高クロム合金の製造方法。

3. 発明の詳細な説明

　この発明は、耐応力腐食割れ性にすぐれ、しかもすぐれた耐応力腐食割れ性が溶接やその後のSR（Stress relief）熱処理によつても低下しないニッケル基高クロム合金の製造方法に関する。

　純水またはCℓ⁻イオンを含む高温高圧環境に使用される化学設備の配管や熱交換器などの材料として、近年30％Cr—60％Ni系合金が注目され、現在その実用化が進められている。30％Cr—60％Ni系は、他の鋼や合金材料に較べ応力腐食割れに対する抵抗性がすぐれる特徴を有しているとの理由からである。この材料のかかる有利性は確か

であるがしかし、この材料を用いてもなお、上記環境下での使用中、溶接熱影響部、更には母材部分にも応力腐食割れ（以下、SCCと略す）の生じる危険は避けられない。これは、成品の製造工程で、または機器組立時の溶接及びその後のSR処理（550℃に20時間程度加熱保持）により、粒界にCrカーバイドが析出して粒界近傍にCr欠乏層が生じ、SCCを生じる結果、30%Cr-60%Ni系本来の性能が損われるためと考えられる。

本発明は、製造直後の成品段階で30%Cr-60%Ni系本来のすぐれた耐SCC性を備えるのはもとより、その後の溶接、SR処理によってもSCCに対し鋭敏化しないNi基合金成品の製造方法を提供しようとするものである。

すなわち本発明は、
①C 0.04%以下、Si 1.0%以下、Mn 1.0%以下、P 0.03%以下、S 0.005%以下、Ni 50～80%、Cr 15～35%、Aℓ 0.50%以下で、必要に応じTi 0.2～1.0%を含み、残部は実質的にFeからなる合金、
②C 0.04%以下、Si 1.0%以下、Mn 1.0%以下、P 0.03%以下、S 0.005%以下、Ni 50～80%、Cr 15～35%、Aℓ 0.50%以下で、Mo 0.5～2.0%、W 0.5～2.0%の一方または双方を含み、更に必要に応じTi 0.2～1.0%を含有し、残部は実質的にFeからなる合金、

上記何れかの合金を、熱間加工後、加工率38%以上で冷間圧延し、引き続き添付図面の第1図に示すA(0.5、850)、B(0.5、750)、C(10、675)、D(100、675)、E(100、850)の5点を結ぶ直線で囲まれる範囲内の加熱温度及び保持時間で最終焼鈍を行うことを特徴とする耐SCC性にすぐれたニッケル基高クロム合金の製造方法、を要旨とする。

30%Cr-60%Ni系合金の場合、板及び管などの成品は一般に、熱間加工後、30%以下の冷延加工を施し、最終熱処理として、加熱温度 950～1100℃、保持時間 2～30分程度の短時間焼鈍を行って製造される。このような鋼種では、SR処理での鋭敏化を避けるため、できるだけ焼鈍後の炭化物の析出を抑えなければならないというのが一

般の常識的な見方である。すなわち、炭化物の析出量が多いと、SR処理によるCrカーバイド析出が加速され、Cr欠乏による鋭敏化の原因となり易いのである。未固溶炭化物の析出は、焼鈍温度が高い程、Cの固溶度が増す関係で、少なくなる。また、焼鈍前の冷間加工についてみれば、加工度が小さい程、炭化物析出の核となるスリップバンドが小さいために炭化物の析出は抑制される傾向となる。このような訳で、30%Cr-60%Ni系合金には、先述の如き製造方法が適用されていたわけであるが、しかしこの方法では焼鈍温度が高くなる関係上、一方では焼鈍の冷却過程において鋭敏化する慮れもあり、更には高温焼鈍を経た成品は、C固溶度の低い温度で実施されるSR処理によって粒界に析出する炭化物の量が多いから、もしCrカーバイドの析出域に入った場合には、確実に鋭敏化してしまうという危険をはらんでいるのである。

しかるに、前記本発明の方法に基いて、焼鈍前の冷間加工を従来より高い加工度にて行うと、合金中には著しく多くのスリップバンドが生じることととなる。ここで、850℃以下、すなわち従来より可成り低目の温度での焼鈍を実施すれば、従来の場合とは全く逆に短時間内で合金中には多量の炭化物が粒内に微細に分散析出することとなる。焼鈍温度を低くするためにCの固溶度が小さくなることによって、炭化物の析出すべき量が多くなるに加え、析出の核となるスリップバンドが予め多量に発生しているため粒内での析出が効果的に促進される結果である。しかもこの場合、鋭敏化の原因になるCrカーバイドの析出についてみれば、多量のスリップバンドによって析出が早められるにつれ、その析出によって生じたCr欠乏層の回復も有効に加速されることになり、このため焼鈍時、第1図のABCラインをこえる程度の比較的短時間内にCr欠乏層の回復は完了する。Cr欠乏層の回復した成品は、少なくともその段階では鋭敏化しておらず、合金本来の高耐SCC性を備えている。

上記により得られた成品をSR処理した場合、更に炭化物が析出するが、この量としてはきわめ

て少なく止められる。すなわち、ＳＲ処理により析出する炭化物の量は、基本的には当該処理温度と前回の焼鈍温度のＣ固溶度の差に比例的であり、従って焼鈍温度が低ければ低い程ＳＲ処理での析出量は少なくなる。また同時に、焼鈍段階で既にＣrカーバイドの折出が十分行なわれていると、析出量は一段と低減されるのである。このようにＳＲ処理による炭化物の析出量が少なく、しかも前記の如く予め合金中に炭化物が微細分散している場合は、たとえＳＲ処理によってＣrカーバイドが析出してもＣr欠乏層は粒内に分散した炭化物の周囲に生じるだけである。本来鋭敏化とは、周知の如く粒界に沿ってＣr欠乏層が連続発生してはじめて起こる現象であり、前記ような分散状態では鋭敏化の懸念は全くない。

　また、前記焼鈍後、溶接とＳＲ処理を受けた場合でも、合金中のＣ量が本発明のように0.04％以下のときには、鋭敏化は避けられる。溶接によって高温に加熱された場合、析出炭化物は再度その加熱温度に対応するＣ固溶度に従って溶け込み、

次のＳＲ処理によって再び析出する軌跡を辿るが、このＳＲ処理の際、Ｃ量が0.04％をこえると、適切な加工及び熱処理を施しても粒界にＣr欠乏層を生じて割れ発生の原因となる。

　以下、本発明における製造条件と使用合金成分限定の理由について説明する。

　第１図は、最終焼鈍における加熱温度と保持時間がＳＲ処理後の耐ＳＣＣ性に及ぼす影響を示す図表である。これは実験により得られたものであるが、実験は基本的には後述の実施例に示す方法に則った。実験に用いた合金は、後述の第１表の成分をもつものであり、冷間加工度としては38％とした。図中、〇：割れ深さ0.05mm未満、×：同じく0.05mm以上、を各々示し、Ａ、Ｂ、Ｃ、Ｄ、Ｅの各点を結んで囲んだところが本発明範囲である。加熱温度が850℃をこえると、Ｃ固溶度が高すぎて焼鈍による炭化物の折出が不十分となり、その後のＳＲ処理での折出量が増し粒界への連続析出による鋭敏化を通して耐ＳＣＣ性が劣化する。他方、675℃を下廻ると、いくら長時間保持でも焼鈍本

米の目的である再結晶が十分達成されない。保持時間については、0.5時間未満では、850℃以下の加熱温度の場合は再結晶が十分進展し得ないとともに、Ｃrカーバイド析出によるＣr欠乏層の回復が不足しＳＲ処理後において耐ＳＣＣ性が低下する。100時間をこえると、経済性の面で不利が大きい。更に、加熱温度675〜850℃、保持時間0.5〜100時間を満たしても、図中Ｂ点（0.5時間、750℃）とＣ点（10時間、675℃）を結ぶ直線ＢＣの下の領域では、再結晶、Ｃr欠乏層の回復がともに不足する。

　第２図は、上記焼鈍前の冷間加工率と合金中Ｃ量の溶接＋ＳＲ処理後の耐ＳＣＣ性に対する影響を示す図である。この結果を得た実験も、前記同様基本的には後述の実施例と同じ方法によったもので、最終焼鈍は800℃×10h、使用合金は第１図の場合と同様である。図中、実線にて囲んだところが本発明範囲を示す。〇、×の表わす意味は、第１図と同じである。冷間加工率は、38％未満では十分な量のスリップバンドが確保し得ず、焼鈍時炭化物が粒内に微細に分散した析出状態が得られな

いとともにＣr欠乏層の回復促進の効果が不足して、前記の如き低温で比較的短時間の焼鈍ではＣr欠乏層の回復が望めないため、溶接＋ＳＲ処理後は云うに及ばず焼鈍後の段階ですでに鋭敏化の懸念がある。冷間加工率が38％以上でも、合金中Ｃ量が多すぎるときは、溶接＋ＳＲ処理後良好な耐ＳＣＣ性が期待できない。一般にＣ量が多い程、焼鈍によって多量の炭化物が得られ易いが、反面、前記冷間加工＋焼鈍によって折出した炭化物が溶接を受けて再度溶け、ＳＲ処理によって再析出する炭化物の量が増し、Ｃrカーバイドの析出による粒界近傍でのＣr欠乏が回避し難くなる。鋭敏化の原因になるこの粒界近傍でのＣr欠乏を防ぐためには、Ｃ量0.04％以下が必要である。

　次に、本発明対象合金の成分限定（Ｃを除く）について記す。

　Ｓi、Ｍn、Ａℓ：何れも脱酸元素であり、各下限値以下では効果がなく、また同じく上限値をこえると、効果が飽和する許りか、合金の清浄度の劣化を来たす。

Ni：耐食性向上の効果著しく、Cℓ⁻を含む高温水中およびアルカリ溶液（NaOH）環境下でのSCCに対する抵抗性を改善する基幹元素であり、50%以上の含有できわめて高い耐食性が期待できる。一方80%をこえるとその効果は飽和し、添加できるCr量が制限を受けるので、80%以下とした。

Cr：Ni同様、耐食性向上に必須の元素である。15%未満では効果が不足し、他方35%をこえると熱間加工性の劣化が著しい。

Ti：炭化物形成元素であり、鋭敏化処理によってCをTiCとして固定するため、有害なCrカーバイドの析出抑制に有効である。0.2%未満ではその効果が十分には期待できず、1.0%を上廻ると合金清浄度の点で問題となる。合金成分中、C、Crが比較的低い合金の場合は、特にTiを添加する必要はない。

Mo、W：これらは不働態皮膜の強化に有効な成分であり、その添加は耐食性改善をもたらす、とくに、濃化Cℓ⁻によるSCCの発生を遅延させるのに効果的であるが、何れも0.5%以上添加しない

とこのような効果の発現はみられず、2.0%をこえると合金の清浄度の悪化を惹起する。

P、S：何れも不純物成分であつて、0.030%をこえると熱間加工性を害する。

次に、本発明の実施例について説明する。

第1表に示す(A)～(G)の各成分をもつ合金を30kg真空溶製し、鍛伸、軟化処理後、第2表に示す各条件にて冷間加工、最終焼鈍を施した。その後更に、550℃、20時間の低温熱処理（SR処理に相当）を施し、またはTIG溶接（ナメ付、60A、フェラーなし）を行なつてからSR処理として上記同様の低温熱処理を施し、これらの材料から2mm厚×10mm巾×75mm長の試験片を2枚ずつ採取した。この2枚の試験片を重ね合せてU字型に曲げ、これをさらに5mm拘束して、いわゆる二重U字曲げ試験片となし、これを3ℓのオートクレーブに貯めた、300PPm Cℓ⁻を含有する非脱気300℃の高温水中に1000時間浸漬した。試験後、U字型の内側の試験片について断面の割れ深さを調査した。結果をまとめて第2表I及びⅡに示す。

第 1 表（wt%）

	合金	C	Si	Mn	Ni	Cr	Ti	W	Mo	Fe
本発明対象材	A	0.020	0.35	0.38	60.13	31.51	0.37	—	—	残
	B	0.032	0.32	0.40	59.78	30.75	0.42	—	—	〃
	C	0.038	0.29	0.37	61.10	31.02	0.38	—	—	〃
	D	0.022	0.31	0.37	60.43	30.27	0.21	1.32	—	〃
	E	0.026	0.29	0.35	61.27	31.14	0.26	—	1.02	〃
比較材	F	0.049	0.31	0.35	60.85	30.07	0.42	—	—	〃
	G	0.060	0.36	1.38	61.37	31.75	0.39	—	—	〃

第 2 表 －I

	No.	合金	冷間加工度 (%)	焼鈍条件 (温度℃×時間h)	SCC最大深さ (mm) 低温熱処理材	溶接+SR処理材
本発明例	1	B	38	850×1	0.01	
	2	B	38	850×10	0.01	
	3	B	38	850×100	0.01	
	4	B	38	800×1	0.02	
	5	B	38	800×10	0.02	
	6	B	38	800×100	0.01	
	7	B	38	750×1	0.02	
	8	B	38	750×10	0.01	
	9	B	38	750×100	0.01	
	10	B	38	675×10	0.01	
	11	B	38	675×100	0.01	
	12	A	38	800×10	0.03	0.01
	13	A	60	800×10	0.02	0.01
	14	B	60	800×10	0.02	0.01
	15	C	38	800×10	0.02	0.02
	16	C	60	800×10	0.03	0.04
	17	D	38	800×10	0.02	
	18	D	38	800×10	0.01	
	19	E	38	800×10	0.02	
	20	E	38	800×100	0.01	
	21	D	60	800×1	0.03	
	22	E	60	800×1	0.02	

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第 2 表 - Ⅱ

No.	合金	冷間加工度 (%)	焼鈍条件 (温度°C×時間)	SCC割れ深さ(mm)	
				低温熱処理材	溶接+SR処理材
23	B	38	850×0.1	0.23	
24	B	38	800×0.1	0.32	
25	B	38	750×0.1	0.38	
26	B	38	700×0.5	0.35	
27	B	38	700×1	0.48	
28	B	38	675×0.5	0.53	
29	B	38	675×1	0.48	
30	B	38	675×5	0.37	
31	D	38	800×0.1	0.25	
32	E	38	800×0.1	0.32	
33	C	20	800×10	—	0.45
34	A	20	800×10	—	0.18
35	B	20	800×10	—	0.25
36	F	20	800×10	—	0.55
37	G	20	800×10	—	0.58
38	F	38	800×10	—	0.39
39	F	60	800×10	—	0.25
40	G	38	800×10	—	0.59
41	G	60	800×10	—	0.43
42	A	30	975×0.5	0.08	0.17
43	B	〃	1000×0.5	0.17	0.30
44	C	〃	1025×0.5	0.29	0.43
45	F	〃	1030×0.5	0.35	0.49
46	G	〃	1050×0.5	0.53	0.63

（No.23〜32：比較例、No.33〜41：比較例、No.42〜46：従来例）

第2表Ⅰ及びⅡにおいて、冷間加工度、焼鈍条件が本発明範囲内のもの(1)〜(22)は、SCCの最大深さが低温熱処理材、溶接+SR処理材の何れの状態ででも0.03mm以下というきわめて小さな値を示した。これに対し、比較例では、(23)〜(32)は焼鈍条件が本発明範囲外のため低温熱処理材でのSCCが本発明例より格段に大きく、また(33)〜(37)は冷間加工度が本発明範囲を下廻るため、溶接+SR処理材の耐SCC性が著しく劣っている。更に(38)〜(41)は、合金中のC量が高すぎて、溶接+SR処理材のSCCが著しくなっている。因みに、常法によって製造した従来例(42)〜(46)より、例え合金中C量を低くしても、低温熱処理材、溶接+SR処理材の耐SCC性は殆んど改善されないことが判る。

以上の説明から明らかなように本発明の製造方法によれば、耐応力腐食割れ性にすぐれた30％Cr−60％Ni系合金のその本来の特性を備えしかもその特性が成品段階のみならず、その後溶接または更にSR処理の影響を受けた場合も良好なまま維持される合金成品を得ることができ、したが

つて本発明は溶接組立される耐食機器に60％Ni−30％Cr合金のすぐれた耐食性能をそのまま生かすことを可能にするという意味で、きわめて利用価値の高い発明ということができる。

4. 図面の簡単な説明

第1図は60％Ni−30％Cr合金の最終焼鈍の加熱温度と保持時間がSR処理後の耐SCC性に及ぼす影響を示す図、第2図は同じく冷間加工度と合金中C量の溶接+SR処理後の耐SCC性に対する影響を表わす図である。
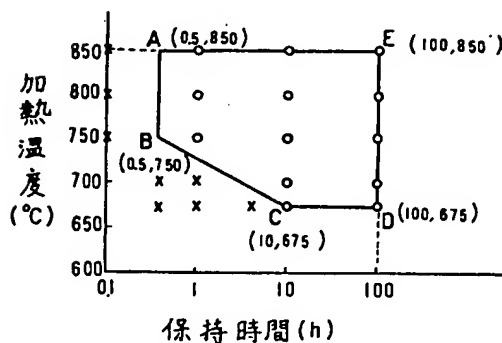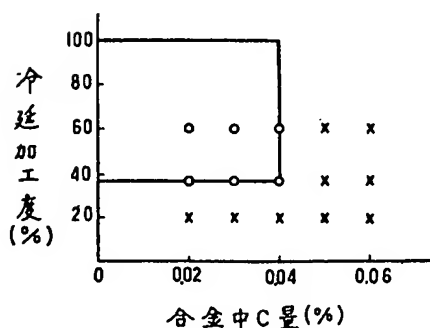
出 願 人 住友金属工業株式会社
代理人弁理士 生 形 元 重

第 1 図

加熱温度(℃)／保持時間(h)
A (0.5,850) E (100,850)
B (0.5,750) C (10,675) D (100,675)

第 2 図

冷延加工度(%)／合金中C量(%)

4/24/2006, EAST Version: 2.0.3.0

PTO 06-3970

METHOD FOR PRODUCING NICKEL-BASE, HIGH-CHROMIUM ALLOY WITH
EXCELLENT RESISTANCE AGAINST STRESS CORROSION CRACKING
[Taioryoku Fushoku Waresei Ni Sugureta Nikkeruki
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SPECIFICATION

1. Title

    METHOD FOR PRODUCING NICKEL-BASE, HIGH-CHROMIUM ALLOY WITH

    EXCELLENT RESISTANCE AGAINST STRESS CORROSION CRACKING

2. Claims

    (1) A method for producing nickel-base, high-chromium alloy with
excellent resistance against stress corrosion cracking, said method
comprising hot-working an alloy that contains not more than 0.04 % C,
not more than 1.0 Si, not more than 1.0 % Mn, not more than 0.03 % P,
not more than 0.005 % S, 50 % to 80 % Ni, 15 to 35 % Cr, and not more
than 0.50 % Al, and, if necessary, 0.2 to 1.0 % Ti, the balance
essentially being Fe, cold-rolling it at a processing degree of 38 %
or more, and subsequently performing final annealing at a heating
temperature and retention time that are within the range defined by
the straight lines that connect the following five points shown in Fig.
1 in the attached drawing: A (0.5, 850), B (0.5, 750), C (10, 675), D
(100, 675), and E (100, 850).

    (2) A method for producing nickel-base, high-chromium alloy with
excellent resistance against stress corrosion cracking, said method
comprising hot-working an alloy that contains not more than 0.04 % C,
not more than 1.0 % Si, not more than 1.0 % Mn, not more than 0.03 % P,
not more than 0.005 % S, 50 % to 80 % Ni, 15 to 35 % Cr, not more than
0.50 % Al, and either or both of 0.5 to 2.0 % Mo and 0.5 to 2.0 % W
and, if necessary, 0.2 to 1.0 % Ti, the balance essentially being Fe,

cold-rolling it at a processing degree of 38 % or more, and subsequently performing final annealing at a heating temperature and retention time that are within the range defined by the straight lines that connect the following five points shown in Fig. 1 in the attached drawing: A (0.5, 850), B (0.5, 750), C (10, 675), D (100, 675), and E (100, 850).

3. Detailed Description of the Invention

The present invention pertains to a method for producing nickel-base, high-chromium alloy that has excellent resistance against stress corrosion cracking and, moreover, that does not lose its excellent resistance against stress corrosion cracking even when it undergoes welding or a subsequent SR (stress relief) heat treatment.

As materials for pipelines, heat exchangers, etc., in chemical facilities that are used in high-temperature, high pressure environments containing pure water or Cl⁻ ions, 30 % Cr-60 % Ni alloys have attracted attention in recent years and are increasingly used for practical applications. This is because 30 % Cr-60 % Ni alloys have superior resistance against stress corrosion cracking compared with other steels and alloy materials. Although this type of alloy material certainly possesses the aforesaid advantage, even this material is not free from the possibility that stress corrosion cracking (hereinafter abbreviated as "SCC") could occur at welding-heat-affected zones--even at the base material portion--during use in the aforesaid type of environment. The reason for this is believed to be that welding and

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the subsequent SR treatment (in which products are maintained at 550 °C for 20 hours or thereabouts) performed in a product manufacturing process or in an equipment assembly process cause Cr carbide to precipitate in grain boundaries, thereby forming Cr-depleted layers and causing SCC; thus, the intrinsic performance of the 30 % Cr-60 % Ni system is deteriorated.

Accordingly, the present invention intends to provide a method for producing Ni-base alloy products that not only have excellent SCC resistance that is intrinsic to the 30 % Cr-60 % Ni system at the stage immediately after their production but also do not become susceptible to SCC even with the subsequent welding or SR treatment.

That is, the gist of the present invention is a method for producing nickel-base, high-chromium alloy with excellent resistance against stress corrosion cracking, said method being characterized by hot-working either one of the alloys described below, cold-rolling it at a processing degree of 38 % or more, and subsequently performing final annealing at a heating temperature and retention time that are within the range defined by the straight lines that connect the following five points shown in Fig. 1 in the attached drawing: A (0.5, 850), B (0.5, 750), C (10, 675), D (100, 675), and E (100, 850),

(1) an alloy that contains not more than 0.04 % C, not more than 1.0 % Si, not more than 1.0 % Mn, not more than 0.03 % P, not more than 0.005 % S, 50 % to 80 % Ni, 15 to 35 % Cr, and not more than

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0.50 % Al, and, if necessary, 0.2 to 1.0 % Ti, the balance essentially being Fe and

(2) an alloy that contains not more than 0.04 % C, not more than 1.0 % Si, not more than 1.0 % Mn, not more than 0.03 % P, not more than 0.005 % S, 50 % to 80 % Ni, 15 to 35 % Cr, not more than 0.50 % Al, and either or both of 0.5 to 2.0 % Mo and 0.5 to 2.0 % W and, if necessary, 0.2 to 1.0 % Ti, the balance essentially being Fe.

Products, such as plates, pipes, etc., that are made from 30 % Cr-60 % Ni alloys are conventionally produced by performing hot working, followed by 30 % or less cold rolling, and, as the final heat treatment, annealing at a heating temperature of from 950 to 1100 °C for a short retention time of 2 to 30 minutes or thereabouts. It is a widely accepted view that, with this type of steel grade, the carbide precipitation after the annealing must be inhibited as much as possible so as to prevent sensitization in the SR treatment. More specifically, a large amount of precipitated carbide causes the CR carbide precipitation by the SR treatment to accelerate and is likely to bring about sensitization caused by Cr depletion. Since the solid solubility of C increases as the annealing temperature becomes higher, the precipitation of non-solid-solution carbide decreases. With respect to the cold working performed before the annealing, the smaller the degree of processing, the fewer the slip bands, which function as the nuclei for the carbide precipitation; consequently, the carbide precipitation tends to be inhibited. For these reasons,

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the production method described in the foregoing has been employed for processing 30 % Cr-60 % Ni alloys. However, because the annealing temperature in this method is high, there is, for one thing, a risk of sensitization in the cooling process of annealing. For another, since the product that has undergone high-temperature annealing contains a large amount of carbide that will be precipitated in the grain boundaries by the SR treatment, which is conducted at a temperature at which the C solid solubility is low, there is the risk that the product is certainly sensitized if the temperature enters the Cr carbide precipitation range.

On the other hand, if, according to the method of the present invention described in the forgoing, the cold working conducted prior to the annealing is implemented with a degree of processing that is higher than that of the existing method, an extremely large number of slip bands are created in the alloy. If, in this condition, annealing is carried out at 850 °C or lower, that is, at a temperature that is considerably lower than the prior art, a large quantity of carbide is dispersed and precipitated finely inside grains in the alloy within a short time, which is exactly the contrary to the case with the prior art. This occurs as a result of the following. Because the annealing temperature is decreased, the C solid solubility decreases, which causes the quantity of carbide to be precipitated to increase. In addition to this, because a large number of slip bands, which function as the nuclei for the precipitation, have been generated, the

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intragranular precipitation is promoted effectively. Furthermore, in this case, with respect to the Cr carbide precipitation, which causes sensitization, as the precipitation is accelerated due to a large number of slip bands, the recovery of the Cr-depleted layers generated by this precipitation is also effectively accelerated; as a result, at the time of annealing, the recovery of the Cr-depleted layers is completed within a relatively short time that slightly exceeds the time indicated by the A-B-C line in Fig. 1. The product in which the Cr-depletion layers have been recovered is not sensitized at least at this stage and exhibits high SCC resistance intrinsic to the alloy.

When the product obtained in the aforesaid manner is subjected to the SR treatment, carbide precipitates further, but the amount of this precipitation can be controlled to an extremely small amount. More specifically, the quantity of the carbide precipitated by the SR treatment is, as a rule, proportional to the difference between the C solid solubility at the temperature of said treatment and that at the preceding annealing temperature; therefore, the lower the annealing temperature, the smaller the precipitation amount in the SR treatment. At the same time, this precipitation amount further decreases if Cr carbide has been deposited sufficiently at the annealing stage. Thus, when the quantity of the carbide precipitated by the SR treatment is small, and, furthermore, when the carbide has been finely dispersed in the alloy, as mentioned before, even if the Cr carbide is precipitated by the SR treatment, the Cr-depleted layers are formed only around the

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carbide that is dispersed in the grains. Sensitization, as is well known, is a phenomenon that occurs only when a Cr-depleted layer is formed continuously along grain boundaries, and, there is no concern for sensitization in the aforesaid dispersed condition.

Even when the product is subjected to welding and an SR treatment after the aforesaid annealing, sensitization can be prevented if the C content in the alloy is not more than 0.04 %, as in the present invention. When the product is heated to a high temperature by welding, the precipitated carbide dissolves again according to the C solid solubility corresponding to the heating temperature and precipitates again in the subsequent SR treatment. In this SR treatment, if the C content exceeds 0.04 %, Cr-depleted layers are formed in the grain boundaries even if proper processing and heat treatment are performed, thus causing cracking.

The following explains the reasons for the production conditions and limits for alloy components set by the present invention.

Fig. 1 is a graph that shows the effect of the heating temperature and retention time of the final annealing on the SCC resistance after the SR treatment. It is created based on experiments, and the experiments were conducted basically in the same manner as the method shown in the working examples described later. The alloys used for the experiments had the components shown in Table 1 presented later, and the degree of cold working was set to 38 %. In the figure, O indicates that the crack depth was less than 0.05 mm, and X

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indicates 0.05 mm or deeper. The range surrounded by the lines that connect A, B, C, D, and E is the range set by the present invention. If the heating temperature exceeds 850 °C, the C solid solubility becomes too high, thus causing insufficient carbide precipitation, and the precipitation quantity in the subsequent SR treatment increases; consequently, sensitization takes place as a result of contiguous precipitation into the grain boundaries, thus deteriorating SCC resistance. On the other hand, if the temperature is below 675 °C, recrystallization, which is the original objective of annealing, cannot be achieved to a satisfactory degree even with a prolonged retention time. As for the retention time, with less than 0.5 hours, recrystallization does not progress sufficiently when the heating temperature is below 850 °C, and the recovery of the Cr-depleted layer by Cr carbide precipitation is insufficient, thereby decreasing SCC resistance after the SR treatment. A retention time exceeding 100 hours is considerably uneconomical. Furthermore, even if the requirements that the heating temperature be from 675 to 850 °C and that the retention time be from 0.5 to 100 hours are met, both recrystallization and recovery of Cr-depletion layers are insufficient in the region below line B-C, which connects point B (0.5 hour, 750 °C) and point C (10 hours, 675 °C) in the figure.

Fig. 2 is a graph that illustrates the effect of the degree of cold working and the C content in the alloy prior to the aforesaid annealing on the SCC resistance after welding + SR processing. The

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experiments from which these results were obtained were, similarly to those described before, also conducted basically according to the same method as in the working examples described later. The final annealing was carried out at 800 °C for 10 hours, and the alloys used here were the same as those described in reference to Fig. 1. In the figure, the range surrounded by the solid lines indicates the range specified by the present invention. O and X have the same meanings as defined in reference to Fig. 1. If the degree of cold working is less than 38 %, a sufficient amount of slip bands cannot be obtained, and a condition in which carbide is finely dispersed in the grains cannot be obtained at the time of annealing. In addition, the effect of promoting the recovery of Cr-depleted layers is not sufficient, and, with the aforesaid type of annealing at a low temperature for a relatively short time, the recovery of Cr-depleted layers cannot be expected, thus presenting a risk of sensitization already after the annealing-- not to mention the welding + SR processing. If the C content in the alloy is too much even if the degree of cold working is 38 % or higher, good SCC resistance after the welding + SR processing cannot be expected. Generally speaking, the larger the C content, the larger the amount of carbide that can be readily obtained by annealing. On the other hand, the carbide precipitated by the aforesaid cold working + annealing is dissolved again by welding, thus increasing the amount of the carbide that is precipitated again by the SR treatment, and this makes it difficult to prevent Cr depletion in the vicinity of the

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grain boundaries caused by the Cr carbide precipitation. In order to prevent this Cr depletion near the grain boundaries, which is the cause of sensitization, the C content must be less than 0.04 %.

The following describes the limits set for the alloy components (excluding C) by the present invention.

Si, Mn, and Al: These are all deoxidizing elements. They do not exert their effects under their lower limits, and, if they exceed their upper limits, not only do their effects reach the maximum, the resulting alloy cleanliness also deteriorates.

Ni: It has a remarkable anticorrosion improving effect, and it is a key element that improves resistance against SCC in high-temperature water containing Cl^- and an alkali solution (NaOH) environment. A content of 50 % or more can be expected to yield extremely high corrosion resistance. On the other hand, if its content exceeds 80 %, its effect reaches the maximum, and it also restricts the amount of Cr that can be added. For these reasons, its content was set to not more than 80 %.

Cr: Like Ni, it is an essential element for anticorrosion improvement. A content of less than 15 % does not yield a sufficient effect, but a content exceeding 35 % causes substantial deterioration of hot workability.

Ti: It is a carbide-forming element, and, because it fixes C in the form of TiC by a sensitization process, it is effective for inhibiting harmful Cr carbide precipitation. A content of less than

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0.2 % does not yield this effect sufficiently, and a content exceeding 1.0 % presents a problem in alloy cleanliness. If, among the alloy ingredients, C and Cr contents are relatively low, it is not essential to add Ti.

Mo and W: These are elements that are effective for fortifying inactive coating, and addition of these elements brings about anticorrosion improvement. They are especially useful for delaying SCC occurrence caused by incrassated Cl^-. However, neither element exhibits this effect unless added in a quantity of 0.5 % or more, but a quantity exceeding 2.0 % brings about deterioration of alloy cleanliness.

P and S: Both are impurities, and a content exceeding 0.030 % adversely affects hot workability.

The following explains working examples of the present invention.

Alloys having compositions (A) through (G) shown in Table 1 were melted in a 30-kg vacuum furnace, forged, and softened, after which they were subjected to cold working and final annealing under the conditions shown in Table 2. Thereafter, they were further subjected to a low-temperature heat treatment at 550 °C for 20 hours (equivalent to the SR treatment) or, alternatively, subjected to TIC welding (Nametsuki [as transliterated], 60A, no feller [as transliterated]) and then, as the SR treatment, to the same low-temperature heat treatment. From each of the materials thus prepared, two test pieces that were 2 mm thick, 10 mm wide, and 75 mm long were obtained. These

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two test pieces were laid one on top of the other and bent in a U-shape, and this structure was further formed into what is called a double U-shaped test piece by keeping 5 mm under restraint. This test piece was immersed for 1000 hours in non-deaerated, 300 °C high-temperature water that contained 300 ppm Cl⁻ and that was stored in a 3 L-capacity autoclave. After the test, the test piece on the inner side of the U-shape was examined to determine the cross-sectional crack depth. A summary of the results is shown in Tables 2-I and II.

TABLE 1 (wt %)

	(c)合金	C	Si	Mn	Ni	Cr	Ti	W	Mo	Fe
(a)本発明対象材	A	0.020	0.35	0.38	60.13	31.51	0.37	—	—	(d)残
	B	0.032	0.32	0.40	59.78	30.75	0.42	—	—	′
	C	0.038	0.29	0.37	61.10	31.02	0.38	—	—	′
	D	0.022	0.31	0.37	60.43	30.27	0.21	1.32	—	′
	E	0.026	0.29	0.35	61.27	31.14	0.26	—	1.02	′
(b)比較材	F	0.049	0.31	0.35	60.85	30.07	0.42	—	—	′
	G	0.060	0.36	1.38	61.37	31.75	0.39	—	—	′

Key: a) materials of the present invention; b) comparative example materials; c) alloys; d) balance.

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TABLE 2-I

	No.	(b) 合金	(c) 冷間加工度 (%)	(d) 焼鈍条件 (温度℃×時間)	(e) SCC 最大深さ (mm)	
					(f) 低温熱処理材	(g) 溶接+SR処理材
(a) 本発明例	1	B	38	850×1	0.01	
	2	B	38	850×10	0.01	
	3	B	38	850×100	0.01	
	4	B	38	800×1	0.02	
	5	B	38	800×10	0.02	
	6	B	38	800×100	0.01	
	7	B	38	750×1	0.02	
	8	B	38	750×10	0.01	
	9	B	38	750×100	0.01	
	10	B	38	675×10	0.01	
	11	B	38	675×100	0.01	
	12	A	38	800×10	0.03	0.01
	13	A	60	800×10	0.02	0.01
	14	B	60	800×10	0.02	0.01
	15	C	38	800×10	0.02	0.02
	16	C	60	800×10	0.03	0.04
例	17	D	38	800×10	0.02	
	18	D	38	800×10	0.01	
	19	E	38	800×10	0.02	
	20	E	38	800×100	0.01	
	21	D	60	800×1	0.03	
	22	E	60	800×1	0.02	

Key: a) examples of the present invention; b) alloy; c) degree of cold working (%); d) annealing conditions (temperature °C x hours); e) SCC maximum depth (mm); f) low-temperature heat treated material; g) welded+SR-treated material.

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TABLE 2-II

	No.	(b) 合金	(c) 冷間加工度 (%)	(d) 焼鈍条件 (温度°C×時間)	(e) SCC割れ深さ(mm)	
					(f) 低温熱処理材	(g) 溶接+SR処理材
(a) 比較例	23	B	38	850×0.1	0.23	
	24	B	38	800×0.1	0.32	
	25	B	38	750×0.1	0.38	
	26	B	38	700×0.5	0.35	
	27	B	38	700×1	0.48	
	28	B	38	675×0.5	0.53	
	29	B	38	675×1	0.48	
	30	B	38	675×5	0.37	
	31	D	38	800×0.1	0.25	
	32	E	38	800×0.1	0.32	
	33	C	20	800×10	—	0.45
	34	A	20	800×10	—	0.18
	35	B	20	800×10	—	0.25
	36	F	20	800×10	—	0.55
	37	G	20	800×10	—	0.58
	38	F	38	800×10	—	0.39
	39	F	60	800×10	—	0.25
	40	G	38	800×10	—	0.59
	41	G	60	800×10	—	0.43
(h) 従来例	42	A	30	975×0.5	0.08	0.17
	43	B	"	1000×0.5	0.17	0.30
	44	C	"	1025×0.5	0.29	0.43
	45	F	"	1030×0.5	0.35	0.49
	46	G	"	1050×0.5	0.53	0.63

Key: a) comparative examples; b) alloy; c) degree of cold working (%);
d) annealing conditions (temperature °C x hours); e) SCC maximum depth
(mm); f) low-temperature heat treated material; g) welded+SR-treated
material; h) conventional examples.

As seen from Tables 2-I and II, with Examples 1 through 22, whose
cold-working degree and annealing conditions were within the ranges
specified by the present invention, the SCC maximum depth was a very
low value of 0.03 mm or less, regardless of whether they were
materials that underwent the low-temperature treatment or materials
that underwent the welding + SR processing. On the other hand, among

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the comparative examples, Examples 23 to 32 showed considerably larger SCC than the present invention because the annealing conditions for these examples were out of the range specified by the present invention. With Examples 33 through 37, because their cold-working degrees were below the range specified by the present invention, the SCC resistance of the materials that underwent the welding + SR processing was considerably deteriorated. Furthermore, because Examples 38 through 41 contained too much C in the alloys, the SCC of the materials that underwent the welding + SR processing deteriorated considerably. Incidentally, from Conventional Examples 42 through 46, which were prepared by the conventional method, it can be seen that, even if the C content in an alloy is reduced, the SCC resistance of a material that is subjected to the low-temperature heat treatment and a material that is subjected to the welding + SR processing is hardly improved.

As is evident from the aforesaid explanation, the production method of the present invention can provide alloy products that have excellent stress corrosion cracking resistance intrinsic to 30 % Cr-60 % Ni alloys and that not only have this excellent property at the stage immediately after they are produced but also retain it after they are subjected to welding or even to an SR treatment. Therefore, the present invention makes it possible to utilize the excellent corrosion performance of 60 % Ni-30 % Cr alloys as is in welded and

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assembled anticorrosive equipment, and, in this respect, the present

invention can be considered to be a highly useful invention.

4.   Brief Explanation of the Drawings

Fig. 1 is a graph that shows the effect of the heating

temperature and retention time of the final annealing of 60 % Ni-30 %

Cr alloy on the SCC resistance after the SR treatment. Fig. 2 is a

graph that illustrates the effect of the degree of cold working and

the C content in the alloy on the SCC resistance after welding + SR

processing.

[FIG. 1]

(a) 加熱温度 (°C)
(b) 保持時間 (h)

[FIG. 2]

(c) 冷延加工度 (%)
(d) 合金中C量(%)
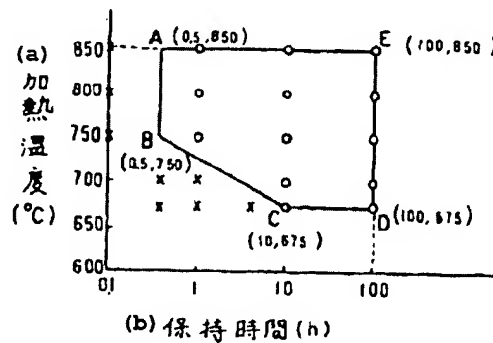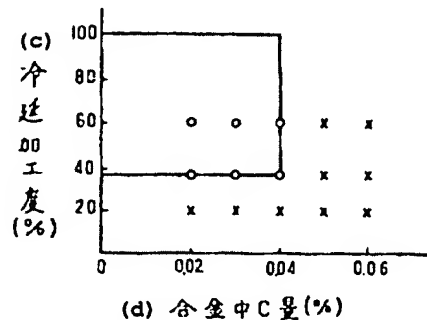
Key: a) heating temperature; b) retention time; c) degree of cold
rolling; d) C content in alloy.